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APPLYING DONNAN THEORY TO EXPLAIN LIGNIN SOLUBILITY DURING CAUSTIC EXTRACTIONS WITH BARIUM CHLORIDE SOLUTIONS

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ABSTRACT

The alkaline extraction stage plays a pivotal role in the removal of residual lignin during bleaching. Previous investigations have shown that lignin extraction efficiency decreases sharply as the $BaCl_2$ concentration in the extraction medium increases from 0.0025 to 0.010 M. However, solubility measurements of oxidized lignin in alkaline $BaCl_2$ solutions predict that lignin extraction efficiency should not have abruptly decreased until the $BaCl_2$ concentration was increased from 0.010 to 0.025 M. We hypothesized that this discrepancy between extraction delignification and lignin solubility is related to a Donnan effect.

A simple Donnan equilibrium model was employed to predict the distribution of mobile ions in the fiber gel system that exists during caustic extraction with $BaCl_2$ solutions. Results from the model suggested that the Ba^{+2} concentration in the interstitial fluid of the fiber should be ~100% higher than the Ba^{+2} concentration in the bulk solution, and ~50% higher than the overall Ba^{+2} concentration applied in the caustic extraction stage. The differences between extraction delignification and lignin solubility were diminished when the delignification data were plotted in terms of the Ba^{+2} concentration of the interstitial fluid and then compared to the corresponding oxidized lignin solubility data.

INTRODUCTION

Many technological developments have been made in the past several decades in order to produce fully bleached chemical pulps with minimum impact on the environment. Some of these advancements have reduced the amount of fresh water required for bleaching and the amount of bleach effluent sent to secondary treatment [1,2]. Since more stringent emission regulations are anticipated, future legislation may require bleach plants to further restrict fresh water usage and minimize effluent emissions.

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One of the major concerns with a low-effluent bleach plant is the build-up of non-process ions [2-4]. The negative influence of certain cations, such as iron, on the chemical reactions that occur during bleaching is well known. Some transition metals can cause the catalytic decomposition of oxygen-based oxidants to unselective radical species, which can attack the carbohydrates in the pulp and cause lower viscosity and strength properties [5-7]. These decomposition reactions can also have a detrimental effect on the brightening reactions, especially with regard to peroxide bleaching [7,8]. It is not as clearly known, however, how non-process metal cations influence the physico-chemical aspects of lignin removal during bleaching.

PREVIOUS BLEACHING STUDIES WITH MULTIVALENT CATIONS

Our previous investigations have shown that high concentrations of Ba^{+2} ions in the alkaline extraction medium (≥0.0025 M) decreased delignification efficiency in the extraction stage (E-stage) [9-11]. We showed that this decreased efficiency was probably related to the lower solubility of oxidized lignin in the presence of Ba^{+2} ions; a similar phenomenon was observed with E-stages conducted in ethanol-water solutions [10-12]. In the solubility study, comparisons were made between the measured lignin solubility and lignin concentration in the E-stage effluents, and the measured post-extraction kappa numbers (Figure 1). The kappa numbers (curve A) and the concentration of lignin, [L], in the effluents (curve B), as shown in this figure, are complementary (i.e., as the kappa decreases, the [L] in the effluent increases). Also plotted in Figure 1 are the solubility limits of the oxidized lignin under alkaline conditions in various $BaCl_2$ solutions (curve C).

We expected the delignification efficiency to abruptly decrease as the $BaCl_2$ concentration in the E-stage was increased from 0.010 to 0.025 M. Instead, extraction delignification sharply decreased as the $BaCl_2$ levels were increased from 0.0025 to 0.010 M. The amount of dissolved lignin in these E-stages did not appear to approach the saturation limits imposed by the solubility of the oxidized lignin. From the data presented in Figure 1, it appeared that lignin solubility was not the only factor restricting extraction efficiency.

We initially proposed that these differences in extraction delignification and lignin solubility could be related to how Ba^{+2} ions are distributed inside and outside the fiber wall [10,11]. In this paper, we develop a Donnan equilibrium model to describe how the ions are partitioned during caustic extraction. We then use the results from this model to

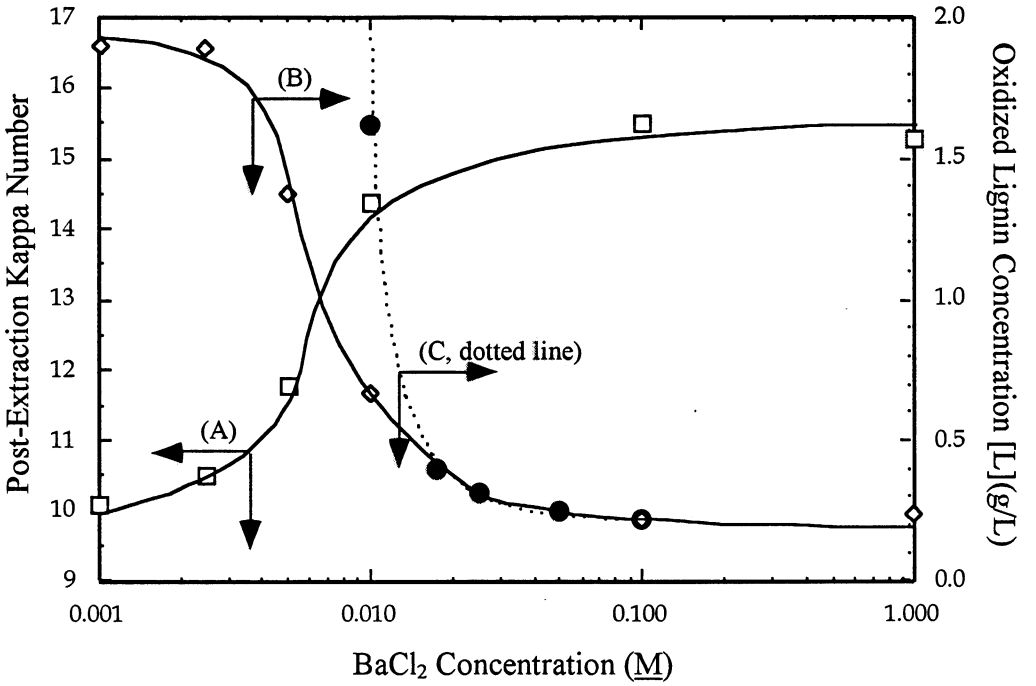


Figure 1. Comparisons of the effect of $BaCl_2$ concentration on post-extraction kappa number (□, curve A), dissolved lignin concentration in the extraction effluents (◇, curve B) and oxidized lignin solubility (●, curve C) [9-11].

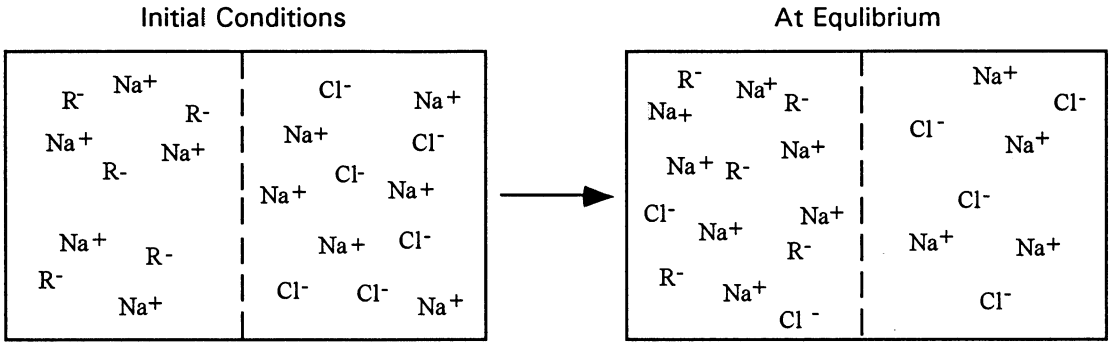
explain the differences observed between lignin solubility and dissolved lignin in E-stage effluents in the presence of Ba^{+2} ions.

REVIEW OF DONNAN EQUILIBRIUM THEORY

Background Information

Donnan theory was originally proposed to describe the partitioning of ionic species between two aqueous solutions separated by a semipermeable membrane [13]. The distribution of diffusable ions in the two solutions, once equilibrium is obtained, will be unequal if one of the solutions contains ions that are unable to diffuse through the membrane (Fig. 2). This effect, known as the Donnan effect, has also been noted with polyelectric gels in aqueous ionic solutions [14-16].

Pulp fibers can be considered polyelectric gels composed of various saccharide monomer units, some of which contain carboxylic acid groups [17,18]. The porous structure of the fiber acts as a semipermeable membrane that allows water and mobile ions to exchange between the interstitial fluid of the fiber and the bulk solution outside the fiber. The ion-


Initial Conditions
At Equlibrium
R-
Na+
Cl-
Na+
Cl-
Na+
R-
Cl-
Na+
Cl-
Na+
Cl-
Na+

$$\lambda = \left(\frac{[X_j^z]_i}{[X_j^z]_o} \right)^{1/z} \tag{1}$$

where $[X_j^z]_i$ and $[X_j^z]_o$ are the concentration of ion X_j inside and outside the gel, respectively; and z is the electrical charge of ion X_j. The above relation is based on the chemical potentials of the ions in the interstitial fluid being equal to the corresponding chemical potentials in the bulk solution after equilibrium has been obtained [13]. Equation 1 assumes that the activity coefficients for ion X_j are approximately the same inside and outside the fiber. Similar approximations have been made by others to simplify the model [17,18,20].

The remaining expressions place constraints on how the mobile ions can diffuse across the semipermeable membrane. Ions cannot pass back and forth between the two solutions to any arbitrary extent. If a cation diffuses through the membrane, then a corresponding anion must also accompany it, such that the entire migrating moiety has a zero net charge [13]. Two sets of equations can be written for the preservation of electrical neutrality inside and outside the cellulose gel:

$$\sum_j z \cdot [X_j^z]_i \; - \; \alpha \cdot [\mathrm{BCA}] \; = \; 0 \tag{2}$$

$$\sum_j z \cdot [X_j^z]_o = 0 \tag{3}$$

where [BCA] represents the bound carboxylic acid groups in the fiber and α is the degree to which the BCA groups are ionized. The BCA anions cause the concentration of cationic species inside the fiber to be higher than their concentration outside the fiber, and vice versa for the concentration of mobile anions. This results in the λ value in Eq. 1 being greater than one.

APPLICATION OF EQUATIONS TO CAUSTIC EXTRACTION

The predominant mobile ions in the E-stages of Figure 1 should be Na^+, Ba^{+2}, HO^- and Cl^-. The highly alkaline conditions of the E-stage results in the overall $[H^+]$ being many orders of magnitude smaller than the $[HO^-]$ ($\sim 10^{-12}$ vs. $\sim 10^{-2}$ M, respectively); thus, the contribution of H^+ ions to the model was neglected in order to simplify the model. Other ions resulting from chlorine dioxide delignification (D_0-stage), such as ClO_2^- and ClO_3^-, were also neglected. The concentration of these ions should be very low since the D_0 pulp was well

washed with deionized water prior to extraction. The [HO^-] value, estimated from the pH of the effluent, was somewhat lower than the initial concentration of alkali applied to the E-stage (~0.071 M NaOH). This lower [HO^-] value was expected due to the neutralization of the carboxylic acids contained in the oxidized lignin.

The high [HO^-] value that exists during extraction virtually assures that the BCA groups will be completely ionized, i.e., $\alpha \approx 1$ in Eq. 2. The amount of BCA in the extracted fibers, ~80 meq/o.d. kg pulp, was ascertained by conductometric titrations. Water retention measurements were performed to determine the amount of interstitial fluid contained in the fibers when soaked in alkaline $BaCl_2$ solutions. An approximate "concentration" of BCA in the fiber was calculated to be 0.0488 M [11] based on the conductometric titration measurements and the water retention value (WRV) of 1.64 mL/o.d. g of pulp [9].

The concentrations of the major ion species present in the caustic extraction performed with $BaCl_2$ solutions were substituted into the electrical neutrality equations (Eqs. 2 and 3) and rearranged in terms of Na^+ ions:

$$[Na^+]_i = [BCA] + [Cl^-]_i + [HO^-]_i - 2 \cdot [Ba^{+2}]_i \tag{4}$$

$$[Na^+]_o = [Cl^-]_o + [HO^-]_o - 2 \cdot [Ba^{+2}]_o \tag{5}$$

Next, the Donnan equilibrium constant λ for Na^+ was defined by substituting Eqs. 4 and 5 into Eq. 1:

$$\lambda = \left(\frac{[Na^+]_i}{[Na^+]_o} \right) = \left(\frac{[BCA] + [Cl^-]_i + [HO^-]_i - 2 \cdot [Ba^{+2}]_i}{[Cl^-]_o + [HO^-]_o - 2 \cdot [Ba^{+2}]_o} \right) \tag{6}$$

The far right-hand side of Eq. 6 was expressed in terms of external concentrations, based on the relation between the internal and external ion concentrations (Eq. 1):

$$\lambda = \left(\frac{[Na^+]_i}{[Na^+]_o} \right) = \left(\frac{[BCA] + [Cl^-]_o / \lambda + [HO^-]_o / \lambda - 2 \cdot \lambda^2 \cdot [Ba^{+2}]_i}{[Cl^-]_o + [HO^-]_o - 2 \cdot [Ba^{+2}]_o} \right) \tag{7}$$

Finally, a simple mass balance for each mobile ion was made for the system:

$$[X_j^z]_o = \left(\frac{[X_j^z]_t \cdot V_t}{V_o + \lambda^z \cdot V_i} \right) \tag{8}$$

where $[X_j^z]_t$ is the total concentration of X_j^z ion in the system; V_o is the aqueous volume outside the fiber; V_i is the interstitial volume of the fiber; and V_t is the total aqueous volume of the system (i.e., $V_t + V_o = V_i$). The values of V_t, V_o and V_i used in Eq. 8 were 0.900, 0.736 and 0.164, respectively; these values were based on the consistency of the E-stage (10%) and the WRV of the pulp in alkaline 0.01 M $BaCl_2$ solutions [9,11].

Equation 7 was solved iteratively with a spreadsheet [11]. A value for λ between 1 and 2 was initially tried. The values for each $[X_j^z]_o$ were calculated from Eq. 8 based on the assumed λ. These calculated concentrations were substituted into Eq. 7 along with the assumed λ and a new λ was determined. The old and new λ values were compared. If the assumed λ was different from the calculated λ, then a new λ was assumed that was between 1 and 2. The above iteration process was repeated until the calculated and assumed λ values converged. Alternative algorithms for solving Donnan models for polyvalent ion systems have been presented by Been and Oloman [18].

The above iterative technique was employed to calculate the distribution of mobile ions with the E-stages shown in Figure 1. The results from the model for selected $BaCl_2$ solutions are given in Table 1. The total concentration of alkali in the E-stage, after the neutralization reactions have occurred, was assumed to be 0.0501 M, based on the 12.7 pH measurement.

DISCUSSION OF THE MODEL'S PREDICTIONS

Overall, the Donnan equilibrium model predicts that the $[Ba^{+2}]_i$ value is ~50% higher than the $[Ba^{+2}]_t$ value and ~100% higher than the $[Ba^{+2}]_o$ value for the E-stages performed with 0.0025 to 0.01 M $BaCl_2$ solutions. It should be pointed out that the calculations presented in Table 1 were based on the water retention value (WRV) of the extracted pulp in alkaline solutions containing 0.01 M $BaCl_2$. This WRV may or may not be representative of E-stages conducted with lower concentrations of $BaCl_2$. Lower concentrations of $BaCl_2$ in the E-stage will cause the pulp to have a higher WRV, as has been observed in an earlier investigation [9]. Calculations were performed with the 0.0025 M $BaCl_2$ E-stage sy-

stem using a WRV for the extracted pulp in the absence of $BaCl_2$ (1.87 mL/o.d. g pulp, [9]). The results from these calculations indicated that small differences in WRV had a negligible effect on the overall ion distribution (Table 2).

Table 1. Donnan model predictions for the partitioning of mobile ions in the fiber gel system for selected E-stages of Figure 1. Calculations are based on [BCA] = 0.0488 M and WRV = 1.64 mL/o.d. g pulp.

E-Stage with 0.0025 M $BaCl_2$; Calculated λ = 1.467			
X_j^z	$[X_j^z]_t$ (M)	$[X_j^z]_o$ (M)	$[X_j^z]_i$ (M)
HO^-	0.0501	0.0532	0.0362
Na^+	0.0501	0.0461	0.0677
Cl^-	0.0050	0.0053	0.0036
Ba^{+2}	0.0025	0.0021	0.0044
E-Stage with 0.005 M $BaCl_2$; Calculated λ = 1.405			
X_j^z	$[X_j^z]_t$ (M)	$[X_j^z]_o$ (M)	$[X_j^z]_i$ (M)
HO^-	0.0501	0.0529	0.0376
Na^+	0.0501	0.0467	0.0655
Cl^-	0.0100	0.0106	0.0075
Ba^{+2}	0.0050	0.0042	0.0084
E-Stage with 0.0100 M $BaCl_2$; Calculated λ = 1.321			
X_j^z	$[X_j^z]_t$ (M)	$[X_j^z]_o$ (M)	$[X_j^z]_i$ (M)
HO^-	0.0501	0.0524	0.0397
Na^+	0.0501	0.0473	0.0625
Cl^-	0.0200	0.0209	0.0158
Ba^{+2}	0.0100	0.0088	0.0154

Table 2. Effect of WRV on the Donnan model predictions for the partitioning of mobile ions in the fiber gel system with 0.0025 M $BaCl_2$ E-stage.

WRV = 1.64 mL/o.d g pulp and [BCA] = 0.0488 M; Calculated λ = 1.467			
X_j^z	$[X_j^z]_t$ (M)	$[X_j^z]_o$ (M)	$[X_j^z]_i$ (M)
HO^-	0.0501	0.0532	0.0362
Na^+	0.0501	0.0461	0.0677
Cl^-	0.0050	0.0053	0.0036
Ba^{+2}	0.0025	0.0021	0.0044
WRV = 1.87 mL/o.d g pulp and [BCA] = 0.0433 M; Calculated λ = 1.408			
X_j^z	$[X_j^z]_t$ (M)	$[X_j^z]_o$ (M)	$[X_j^z]_i$ (M)
HO^-	0.0501	0.0533	0.0379
Na^+	0.0501	0.0462	0.0650
Cl^-	0.0050	0.0053	0.0038
Ba^{+2}	0.0025	0.0021	0.0042

A second factor that was ignored in the above Donnan model was the effect of oxidized lignin on the distribution ions. Some of the oxidized lignin remains inside the pulp fibers due to its insolubility in aqueous solutions containing Ba^{+2} ions. This insoluble lignin contains carboxylic acid functional groups [21] that contribute to the total amount of BCA groups inside the fiber. The contribution of the insoluble lignin to the BCA values in Table 1 could not be ascertained since the Ba^{+2} insoluble lignin is solubilized during the conductometric titration measurement. It is expected that the inclusion of carboxylic acids from the insoluble lignin to the [BCA] value would cause the $[Ba^{+2}]_i$ values to be higher than those shown in Table 1.

The effect of insoluble lignin on the distribution of ions was hypothetically examined for the 0.005 M $BaCl_2$ E-stage. The total concentration of BCA for this pulp was roughly estimated to be 0.0644 M (Table 3). Overall, the increase in $[BCA^-]$ from the insoluble lignin caused the $[Ba^{+2}]_i$ value to be twice the $[Ba^{+2}]_t$ value. This result indicates that the presence of insoluble oxidized lignin inside the fiber further intensifies the Ba^{+2} concentration gradient between the interstitial and bulk solutions in the cellulose gel.

Table 3. Effect of BCA on the Donnan model predictions for the partitioning of mobile ions in the fiber gel system with 0.0050 M $BaCl_2$ E-stage. Calculations are based on WRV = 1.64 mL/o.d. g pulp.

[BCA] = 0.0488 M; Calculated λ = 1.405			
X_j^z	$[X_j^z]_t$ (M)	$[X_j^z]_o$ (M)	$[X_j^z]_i$ (M)
HO^-	0.0501	0.0529	0.0376
Na^+	0.0501	0.0467	0.0655
Cl^-	0.0100	0.0106	0.0075
Ba^{+2}	0.0050	0.0042	0.0084
[BCA] = 0.0644 M; Calculated λ = 1.739			
X_j^z	$[X_j^z]_t$ (M)	$[X_j^z]_o$ (M)	$[X_j^z]_i$ (M)
HO^-	0.0501	0.0543	0.0312
Na^+	0.0501	0.0442	0.0768
Cl^-	0.0100	0.0108	0.0062
Ba^{+2}	0.0050	0.0037	0.0110

The apparent discrepancy between extraction efficiency and lignin solubility depicted in Figure 1 is likely a result of the Donnan effect. A higher Ba^{+2} concentration inside the fiber lowers solubility of oxidized lignin in the interstitial fluid and, thus, limits lignin dissolution and extraction from the fiber wall. To test this hypothesis, we replotted the kappa numbers and dissolved lignin concentrations of the E-stages of Figure 1 in terms of $[Ba^{+2}]_i$

calculated by the simple Donnan model of Table 1. The results were then compared to the corresponding solubility data (Figure 3).

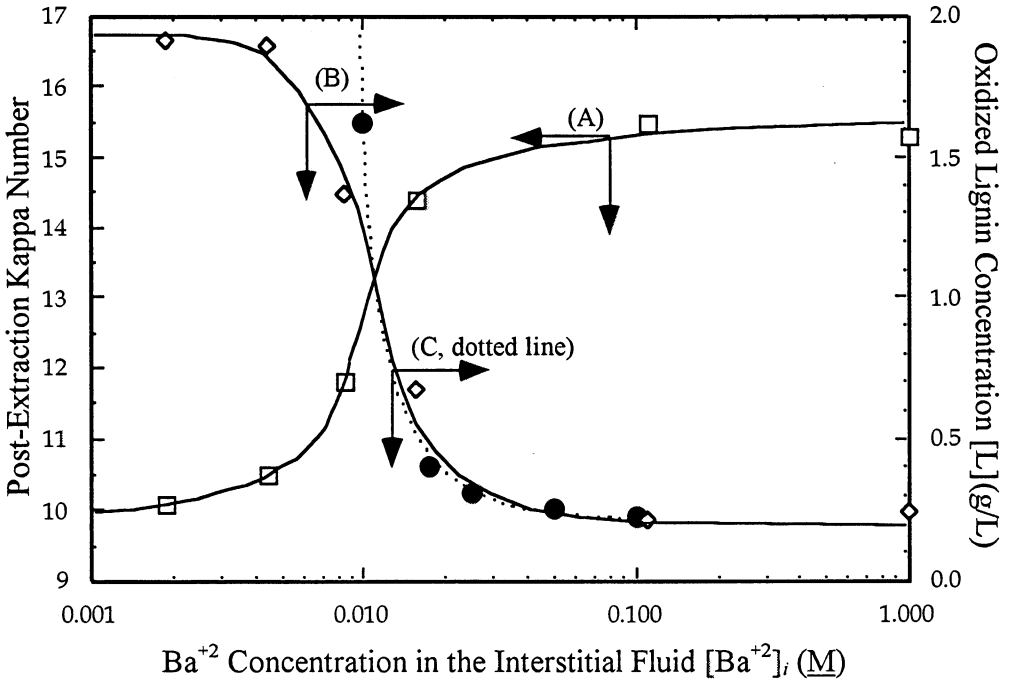


Figure 3. Comparisons of the effect of Ba^{+2} concentration in the interstitial fluid of the fiber on post-extraction kappa number (□, curve A), dissolved lignin concentration in the extraction effluents (◇, curve B) and oxidized lignin solubility (●, curve C).

The sharp decrease in the dissolved lignin concentration and kappa number reduction (curves B and A, respectively) matched more closely the rapid changes in lignin solubility (curve C) when the E-stage delignification data were plotted in terms of $[Ba^{+2}]_i$. The information in Figure 3 strongly suggests that the dissolution of oxidized lignin into the interstitial fluid and it subsequent removal from the fiber is limited when $[Ba^{+2}]_i \geq 0.01$ M. Greater reconciliation of the delignification and solubility data could be obtained if the above model was modified to include the effects of insoluble oxidized lignin on $[Ba^{+2}]_i$ value; however, this simplistic Donnan model provided an adequate estimate for $[Ba^{+2}]_i$.

PRACTICAL IMPLICATIONS FROM THIS STUDY

In general, the results from this study and earlier research [9-12] show that Ba^{+2} has a negative effect on lignin removal in alkaline extraction stages. The observed phenomenon

with Ba^{+2} ions is a complex interaction between the solubility of oxidized lignin, and the Donnan effect exerted by the bound carboxylic acids and the insoluble lignin in the fiber. The concentrations of Ba^{+2} ions during bleaching are expected to rise as bleach plants further restrict their fresh water usage and minimize their effluent emissions in the future. However, it is unlikely that Ba^{+2} ions will reach the critical concentration levels of 10^{-3} to 10^{-2} M observed in this study; Ba^{+2} forms insoluble complexes with SO_4^{-2} and $C_2O_4^{-2}$, which are also present in the bleach mill's process streams [3,4,22].

Additional research is needed to determine if other multivalent cations or combinations of multivalent cations have a detrimental effect on lignin removal during caustic extraction. Such information will be useful to determine the maximum concentration of non-process cations that can be tolerated without impacting the physico-chemical aspects of bleaching delignification in the low-effluent bleach plants of the future.

CONCLUSIONS

A Donnan equilibrium model predicts that the $[Ba^{+2}]$ value inside the fiber should be substantially higher than the $[Ba^{+2}]$ value outside the fiber and that the distribution of mobile ions in the fiber gel model will be unaffected by the small changes in the interstitial volume of the gel as the $[Ba^{+2}]$ in the extraction medium increases from 0 to 0.01 M. The residual oxidized lignin inside the fiber can increase the concentration of immobile carboxylic anions in the interstitial fluid which further intensifies the $[Ba^{+2}]$ gradient projected by the Donnan model.

The apparent differences between caustic extraction efficiency and lignin solubility we observed in earlier studies are likely the result of the Donnan effect. The differences between extraction delignification and lignin solubility were diminished when the E-stage delignification data were plotted in terms of the Ba^{+2} concentration of the interstitial fluid as predicted by the Donnan model.

Additional studies are needed to evaluate how oxidized lignin solubility and extraction delignification are affected by other multivalent cations. The build-up of these cations in low-effluent bleach plants may decrease bleaching delignification by lowering the solubility limit of oxidized lignin in the interstitial fluid of the fiber.

EXPERIMENTAL PROCEDURES

A conventional kraft pulp (southern pine) was obtained from a mill and used throughout this study. Additional details about the pulping conditions are provided in previous reports [9,11]. The D_0-stage was performed on a 29.3 kappa pulp at the following conditions: 1.79% ClO_2 on o.d. pulp (0.16 kappa factor), 3% consistency (100% aqueous), initial pH 4.2-4.6 prior to ClO_2 addition, 45°C, 30 minutes reaction time, and an end pH of 2.4. This treatment yielded a pulp with a kappa number of 19.5.

General caustic extraction conditions were as follows: 2.58% NaOH on pulp (0.55 caustic multiple), 10% consistency, 60°C, and 60 minutes reaction time. Extractions were performed in Kapak®/Scotchpack heat-sealable pouches with various media [9,11]. After extraction, the effluents were separated from the pulp fibers (prior to washing), placed in an amber reagent bottle, and stored at 5°C until needed. The pulps were washed with 130 mL/o.d. g of pulp of the corresponding medium (without alkali). Residual lignin content in the pulps was determined by micro-kappa number measurements (TAPPI Useful Method UM-246).

Methods for measuring the amount of dissolved lignin in the extraction effluents and for measuring oxidized lignin solubility in various $BaCl_2$ solutions have been given in a previous report [10,11]. The amount of BCA groups in an aqueous DE bleached pulp [11] was ascertained by the conductometric titration method described by Katz *et al.* [23]. Details of the measurement of water retention values of extracted pulps soaked in various electrolytic solutions have been reported in an earlier study [9,11].

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